

Theory of the ground state spin of the NV^- center in diamond: I. Fine structure, hyperfine structure, and interactions with electric, magnetic and strain fields

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The ground state spin of the negatively charged nitrogen-vacancy center in diamond has been the platform for the recent rapid expansion of new frontiers in quantum metrology and solid state quantum information processing. In ambient conditions, the spin has been demonstrated to be a high precision magnetic and electric field sensor as well as a solid state qubit capable of coupling with nearby nuclear and electronic spins. However, in spite of its many outstanding demonstrations, the theory of the spin has not yet been fully developed and there does not currently exist thorough explanations for many of its properties, such as the anisotropy of the electron g-factor and the existence of Stark effects and strain splittings. In this work, the theory of the ground state spin is fully developed for the first time using the molecular orbital theory of the center in order to provide detailed explanations for the spin's fine and hyperfine structures and its interactions with electric, magnetic and strain fields.

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I. INTRODUCTION

The negatively charged nitrogen-vacancy (NV^-) center is a unique defect in diamond that has many promising applications in quantum metrology and quantum information processing (QIP). In particular, the ground state spin has been used in recent demonstrations of high precision magnetic^{1–8} and electric field⁹ sensing, as well as spin-photon¹⁰ and spin-spin^{11–15} entanglement. The NV^- center has also been employed to explore the developing decoherence based sensing techniques.^{16–19} Each of these demonstrations exploit the interaction of the spin with some configuration of electric, magnetic and strain fields and the center's remarkable capability of optical spin-polarization and readout.^{20,21} The demonstration of electric field sensing,⁹ which required the precise control of the spin using magnetic fields and the intricate modeling of the spin's interaction with electric, magnetic and strain fields, highlighted the NV^- center as a universal field sensor at the nanoscale as well as emphasized the requirement for a more detailed theoretical understanding of this important spin in diamond. The development of such an understanding will enable more precise control and modeling of the spin in its current applications and also provide the necessary insight to explore its future applications.

The NV^- center is a point defect of C_{3v} symmetry in diamond consisting of a substitutional nitrogen atom adjacent to a carbon vacancy (refer to Fig. 1). The center's electronic structure is summarized in Fig. 2. It consists of a 3A_2 ground triplet state, an optical 3E excited triplet and several dark singlet states.²² The fine structure of the 3E excited triplet is highly dependent on temperature²³

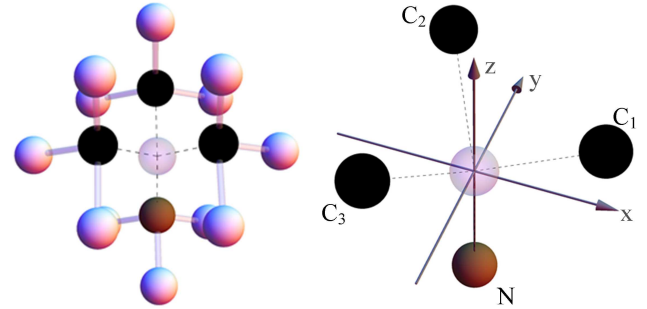


FIG. 1: (color online) Schematics of the nitrogen-vacancy center and lattice depicting the vacancy (transparent), the nearest-neighbor carbon atoms to the vacancy (black), the substitutional nitrogen atom (brown), and the next-to-nearest carbon neighbors to the vacancy (white). The adopted co-ordinate system and carbon labels are depicted in the right schematic.

and crystal strain,²⁴ whereas the fine structure of the 3A_2 ground triplet state is observed to be only weakly dependent on temperature²⁵ and crystal strain with a single zero-field splitting of $D_{gs} \sim 2.87$ GHz between the $m_s = 0$ and $m_s = \pm 1$ spin sub-levels. At ambient temperatures, the fine structure of the excited triplet state replicates the ground triplet state with a single zero-field splitting of $D_{es} \sim 1.42$ GHz^{26,27} independent of crystal strain due to the dynamic Jahn-Teller effect.²³ Zeeman and Stark splittings have been observed in the fine structures of both triplet states,^{26,28–30} although the Stark effect in the ground triplet state is several orders of magnitude smaller than in the excited triplet state.^{29,30}

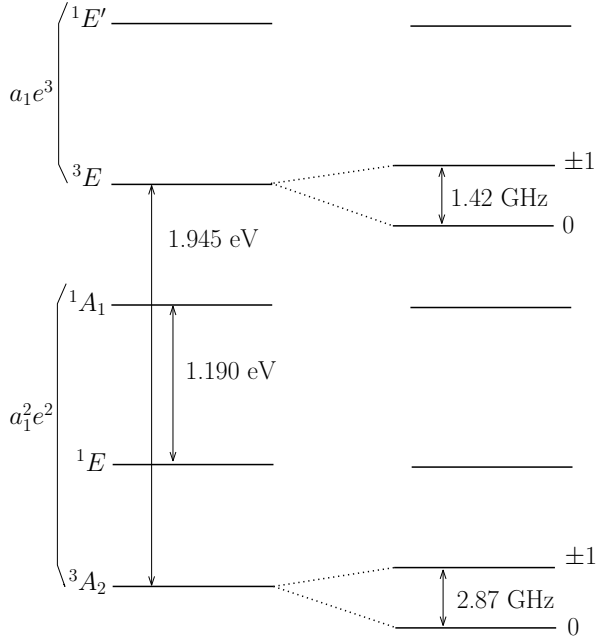


FIG. 2: The electronic orbital structure (left) and fine structure (right) at ambient temperatures formed from the ground $a_1^2e^2$ and first excited a_1e^3 molecular orbital configurations. The observed optical zero phonon line (1.945 eV)³¹ and infrared zero phonon line (1.190 eV)³² transitions are depicted as solid arrows in the orbital structure.

Electron spin resonance (ESR)³³ and *ab initio* studies^{34–42} have confirmed that the electronic states of the center are highly localized to the vacancy and its nearest neighbors. The localization of the center's electronic states supports the application of a molecular model, in which the center's states are approximated by configurations of molecular orbitals (MOs). The molecular model has been successfully applied to describe the effects of electric, magnetic and strain fields on the fine structure of the excited triplet state,^{24,26,29} however the model has not yet been applied to describe the effects of the fields on the ground triplet state. This has been due to an absence of the spin-orbit and spin-spin induced couplings of the center's electronic states, which have been obtained recently in Ref. 22. Consequently, until now, the measurements of the effects of the fields on the ground state spin have been interpreted using the effective spin-Hamiltonian formalism of ESR.^{30,33,43,44} Whilst the spin-Hamiltonian formalism has provided a practical model for the implementation of the center's applications to date, it does not facilitate the correlation of the properties of the ground state spin to the other properties of the center nor the theoretical prediction of more intricate properties of the spin. Consequently, the application of the molecular model to describe the effects of electric, magnetic and strain fields on the ground state spin is expected to provide the required detailed theoretical understanding of the spin.

In this article, the well established molecular model^{22,43,47,48} of the NV⁻ center will be applied in order to fully develop the theory of the ground state spin. The fine and hyperfine structure and their corresponding eigenstates will be constructed prior to examining the effect of electric, magnetic and strain fields on each. By using the matrix representations derived in the recently published electronic solution,²² explicit expressions in terms of the center's MOs will be derived in this work for the hyperfine interaction with the ¹⁴N nucleus, the components of the electron g-factor tensor, and the Stark and strain interactions. The derivation of these expressions enables the rigorous definition of the spin-Hamiltonian of the ground state spin and the correlation of the accurately measured parameters of the spin to the other observed properties of the center. The expressions will also assist future *ab initio* studies to independently calculate the properties of the ground state spin.

II. ELECTRONIC FINE STRUCTURE AND INTERACTIONS WITH ELECTRIC, MAGNETIC AND STRAIN FIELDS

By adopting the adiabatic approximation and considering the nuclei of the crystal to be fixed at their equilibrium coordinates \vec{R}_0 corresponding to the ground electronic state, the electronic Hamiltonian \hat{H}_e of the NV⁻ center can be defined as

$$\begin{aligned} \hat{H}_e = & \sum_i \hat{T}_i + \hat{V}_{Ne}(\vec{r}_i, \vec{R}_0) + \hat{V}_{so}(\mathbf{x}_i, \vec{R}_0) + \hat{V}_{hf}(\mathbf{x}_i, \mathbf{X}_0) \\ & + \sum_{i>j} \hat{V}_{ee}(\mathbf{x}_i, \mathbf{x}_j) + \hat{V}_{ss}(\mathbf{x}_i, \mathbf{x}_j) \end{aligned} \quad (1)$$

where $\mathbf{x}_i = (\vec{r}_i, \vec{s}_i)$ denotes the collective spatial and spin coordinates of the i^{th} electron of the center, $\mathbf{X}_0 = (\vec{R}_0, \vec{I})$ denotes the collective equilibrium spatial and spin coordinates of the crystal nuclei, \hat{T}_i is the kinetic energy of the i^{th} electron, \hat{V}_{Ne} is the effective Coulomb potential of the interaction of the nuclei and lattice electrons with the electrons of the center, \hat{V}_{so} is the electronic spin-orbit potential, \hat{V}_{hf} is the hyperfine potential of the interactions between the crystal nuclei and the electrons of the center, \hat{V}_{ee} is the Coulomb repulsion potential of the electrons of the center and \hat{V}_{ss} is the electronic spin-spin potential.

Ab initio studies^{34–42} have confirmed the presence of three MOs (a_1 , e_x , e_y) in the band gap of diamond and the center's observable electronic structure has been shown to consist of the ground $a_1^2e^2$ and first excited a_1e^3 MO configurations formed from the occupation of the MOs by four electrons.²² Note that the other two electrons of the six electrons associated with the center occupy delocalized A_1 symmetric MOs within the diamond valence band and do not influence the observable properties of the center. The electronic states can be constructed by firstly defining orbital states with well defined C_{3v} orbital symmetry formed from products of the

MOs and defining spin states with well defined C_{3v} spin symmetry.²² Secondly, electronic states $\Phi_{n,j,k}^{so}$ that transform as specific rows k of irreducible representations j of the C_{3v} group in spin-orbit space are formed from linear combinations of the orbital and spin state products.²² Note that the quantum number n denotes the fine structure level of the electronic state. For example, using the irreducible representations contained in Ref. 47, the electronic states of the ground triplet are

$$\begin{aligned}\Phi_{1,A_1}^{so} &= \Phi_{A_2} S_{A_2} = \frac{1}{\sqrt{2}}(|a_1 \bar{a}_1 e_x \bar{e}_y\rangle + |a_1 \bar{a}_1 \bar{e}_x e_y\rangle) \\ \Phi_{2,E,x}^{so} &= -\Phi_{A_2} S_{E,y} = \frac{1}{\sqrt{2}}(|a_1 \bar{a}_1 e_x e_y\rangle - |a_1 \bar{a}_1 \bar{e}_x \bar{e}_y\rangle) \\ \Phi_{2,E,y}^{so} &= \Phi_{A_2} S_{E,x} = \frac{-i}{\sqrt{2}}(|a_1 \bar{a}_1 e_x e_y\rangle + |a_1 \bar{a}_1 \bar{e}_x \bar{e}_y\rangle)\end{aligned}\quad (2)$$

where $\Phi_{A_2} = \frac{1}{\sqrt{2}}(a_1 a_1 e_x e_y - a_1 a_1 e_y e_x)$ is the A_2 orbital state of the ground triplet, the kets on the right hand side denote Slater determinants (overbar denoting down-spin), and the symmetrised $S = 1$ spin states in terms of the S_z eigenstates $\{|S, m_s\rangle\}$ are $S_{A_2} = |1, 0\rangle$, $S_{E,x} = \frac{-i}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle)$ and $S_{E,y} = \frac{-i}{\sqrt{2}}(|1, 1\rangle - |1, -1\rangle)$.

The majority of the spin-orbit states $\Phi_{n,j,k}^{so}$ are eigenstates of the orbital components of the electronic Hamiltonian $\hat{H}_o = \sum_i \hat{T}_i + \hat{V}_{Ne}(\vec{r}_i, \vec{R}_0) + \sum_{i>j} \hat{V}_{ee}(\mathbf{x}_i, \mathbf{x}_j)$ with orbital energies denoted by $E_{J,S}$ (where to remain consistent with Ref. 22, J denotes the irreducible representation of the orbital state and S denotes the total spin of the spin states used to form $\Phi_{n,j,k}^{so}$ and the orbital energy of the ground triplet is defined as $E_{A_2,1} = 0$). Only the spin-orbit states ($\Phi_{3,E,x}^{so}, \Phi_{3,E,y}^{so}, \Phi_{9,E,x}^{so}, \Phi_{9,E,y}^{so}$) associated with the 1E and $^1E'$ singlets are not eigenstates of \hat{H}_o and are mixed by the Coulomb coupling coefficient κ (refer to Ref. 22 for further details). The energies $E_{J,S}$ including the effects of the Coulomb repulsion of the E singlets form the orbital structure of the center depicted in Fig. 2.

The electronic spin-orbit and spin-spin potentials can be treated as first-order perturbations to \hat{H}_o using the orbital energies $E_{J,S}$ and the spin-orbit states $\Phi_{n,j,k}^{so}$ (accounting for Coulomb coupling) as the zero-order energies and states of the perturbation expansion. The perturbed energies correct to first-order E_n have been shown to be consistent with the observed fine structure of the center depicted in Fig. 2.²⁴ It is found that the fine structure of the ground triplet state is governed by electronic spin-spin interaction which splits the $m_s = 0$ and $m_s = \pm 1$ spin sub-levels such that $E_2 - E_1 = D_{gs} \sim 2.87$ GHz, where

$$D_{gs} = \frac{3\mu_0 g_e^2 \mu_B^2}{8\pi} \langle e_x(\vec{r}_1) e_y(\vec{r}_2) | \frac{1 - 3z_{12}^2/|\vec{r}_{12}|^2}{|\vec{r}_{12}|^3} (|e_x(\vec{r}_1) e_y(\vec{r}_2)\rangle - |e_y(\vec{r}_1) e_x(\vec{r}_2)\rangle), \quad (3)$$

μ_0 is the vacuum permeability, $g_e = 2.0023$ is the free electron g-factor, μ_B is the Bohr magneton, $\vec{r}_i = x_i \vec{x} + y_i \vec{y} + z_i \vec{z}$ ($\vec{x}, \vec{y}, \vec{z}$ being unit coordinate vectors), $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$, and $z_{12} = z_2 - z_1$. As obtained in Ref. 22,

TABLE I: The spin coupling coefficients of the ground triplet correct to first-order in spin-orbit and spin-spin interactions. The Coulomb coupling coefficient κ , the spin-orbit parameters (λ_{\parallel} , λ_{\perp}), the spin-spin parameters ($D_{1,E,1}, D_{1,E,2}$), and the spin-spin coupling coefficient of the excited triplet η are as defined in Ref. 22. Note that $N_{\kappa} = (1 + |\kappa|^2)^{-1/2}$.

| |
|--|
| $s_{1,4} = -2i \frac{\lambda_{\parallel}}{E_{A_2,1;0}}$ |
| $s_{1,8} = -\sqrt{2} \frac{\lambda_{\perp} + D_{1,E,2}}{E_{E,1}}$ |
| $s_{2,3} = iN_{\kappa} \kappa \frac{\lambda_{\perp}}{E_{E,0}}$ |
| $s_{2,5} = -\sqrt{2} \frac{D_{1,E,1}}{E_{E,1}} - \eta \frac{\lambda_{\perp} - D_{1,E,2}}{E_{E,1}}$ |
| $s_{2,6} = \frac{\lambda_{\perp} - D_{1,E,2}}{E_{E,1}} - \sqrt{2} \eta \frac{D_{1,E,1}}{E_{E,1}}$ |
| $s_{2,9} = -iN_{\kappa} \frac{\lambda_{\perp}}{E_{E',0}}$ |

the first-order corrected spin-orbit states $\Phi_{n,j,k}^{so'}$ have the general form

$$\Phi_{n,j,k}^{so'} = N_n \left(\Phi_{n,j,k}^{so} + \sum_{m \neq n} s_{n,m} \Phi_{m,j,k}^{so} \right) \quad (4)$$

where N_n are normalization constants and $s_{n,m}$ are the first-order spin coupling coefficients. Using the results of Ref. 22, the first-order spin-orbit states of the ground triplet are

$$\begin{aligned}\Phi_{1,A_1}^{so'} &= \Phi_{1,A_1}^{so} + s_{1,4} \Phi_{4,A_1}^{so} + s_{1,8} \Phi_{8,A_1}^{so} \\ \Phi_{2,E,k}^{so'} &= \Phi_{2,E,k}^{so} + s_{2,3} \Phi_{3,E,k}^{so} + s_{2,5} \Phi_{5,E,k}^{so} \\ &\quad + s_{2,6} \Phi_{6,E,k}^{so} + s_{2,9} \Phi_{9,E,k}^{so}\end{aligned}\quad (5)$$

where $k = x, y$ and the spin coupling coefficients of the ground triplet are contained in table I and are functions of the orbital energies $E_{J,S}$, the axial $\lambda_{\parallel} = 5.3$ GHz²⁴ and non-axial $\lambda_{\perp} \sim$ GHz spin-orbit parameters, the spin-spin parameters $D_{1,E,1} \sim$ MHz and $D_{1,E,2} \sim$ MHz, the Coulomb coupling coefficient κ , and the spin-spin coupling coefficient of the excited triplet $\eta = 0.053$.²²

Note that recent strain measurements of the infrared zero phonon line (ZPL)⁴⁹ have indicated that the Coulomb coupling coefficient is significant $\kappa \sim 0.3$ and therefore must be retained to second-order in the spin coupling coefficients. Furthermore, it should be noted that since the spin-orbit and spin-spin parameters are expected to be of the order of $\sim 10^{-9}$ - 10^{-6} eV (MHz-GHz) and the orbital energies are expected to be of the order of $\sim 10^{-2} - 10^1$ eV, the spin coupling coefficients are expected to be of the order of $10^{-4} - 10^{-10}$. The relative magnitudes of the different coefficients will become important in determining the leading order terms that contribute to the interactions of the ground state spin with electric, magnetic and strain fields.

Given (5) and the zero-order orbital and spin operator matrix representations contained in Ref. 22, matrix representations of the ground triplet using the basis of first-order corrected spin-orbit states $\{\Phi_{1,A_1}^{so'}, \Phi_{2,E,x}^{so'}, \Phi_{2,E,y}^{so'}\}$

can be constructed for general one-electron orbital tensor operators $\hat{O}_{p,q} = \sum_i \hat{O}_{p,q}(\vec{r}_i)$, which transform as the row q of the irreducible representation p of the C_{3v} group, and the total spin operator $\vec{S} = \sum_i \vec{s}_i$ (see table II). The matrix representations are expressed in their most simplified form in terms of one-electron reduced matrix elements and the center's MOs. The one-electron matrix elements and the associated reduced matrix elements are related by the Wigner-Eckart theorem⁵⁰

$$\langle \phi_{f,g}(\vec{r}_1) | \hat{O}_{p,q}(\vec{r}_1) | \phi_{j,k}(\vec{r}_1) \rangle = \begin{pmatrix} j & p \\ k & q \end{pmatrix}^* \langle \phi_f | \hat{O}_p | \phi_j \rangle \quad (6)$$

where $\phi_{j,k}$ and $\phi_{f,g}$ are MOs of symmetry (j,k) and (f,g) respectively, and $\begin{pmatrix} j & p \\ k & q \end{pmatrix}$ are the Clebsch-Gordon coefficients defined in Ref. 47. The detailed model of the interactions of the ground state spin with electric, magnetic and strain fields can thus be developed by applying the matrix representations of table II to each interaction in turn. As a result, the interactions will be expressed in their most simplified form in terms of the spin coupling coefficients, the MOs, and the reduced matrix elements.

A. Interactions with magnetic fields

Defining \vec{B} to be the applied magnetic field that is assumed to be approximately constant over the dimensions of the NV⁻ center, the interaction of the center's electrons with the magnetic field is described by the potential⁵¹

$$\hat{V}_{\text{mag}} = \frac{\mu_B}{\hbar} \sum_i (\vec{l}_i + g_e \vec{s}_i) \cdot \vec{B} + \frac{1}{2m_e c^2} (\vec{s}_i \times \vec{\nabla} \hat{V}_{Ne}(\vec{r}_i)) \cdot (\vec{B} \times \vec{r}_i) \quad (7)$$

where $\vec{l} = l_x \vec{x} + l_y \vec{y} + l_z \vec{z} = \vec{r} \times \vec{p}$ is the electron orbital magnetic moment, \vec{p} is the electron momentum, \hbar is the reduced Planck constant, m_e is the mass of an electron and c is the speed of light. Note that the origin of the coordinate system is defined to be at the center of the NV⁻ defect, in the vicinity of the vacancy (as depicted in Fig. 1). Additionally, note that the term $\sum_i \frac{e^2}{8m_e} (\vec{B} \times \vec{r}_i)^2$ (where e is the electronic charge) quadratic in the magnetic field⁵¹ has been neglected in the above definition since it does not induce a relative shift of the fine structure levels or couple the electronic states of the ground triplet at first-order in the spin coupling coefficients. The second term in (7) arises from relativistic corrections to the non-relativistic first term⁵¹ and can be written in the more explicit form

$$\frac{1}{2m_e c^2} (\vec{s} \times \vec{\nabla} \hat{V}_{Ne}) \cdot (\vec{B} \times \vec{r}) = \frac{1}{2m_e c^2} \vec{s} \cdot \vec{G} \cdot \vec{B} \quad (8)$$

where the orbital operator \vec{G} is the matrix

$$\begin{pmatrix} \frac{\partial \hat{V}_{Ne}}{\partial y} y + \frac{\partial \hat{V}_{Ne}}{\partial z} z & -\frac{\partial \hat{V}_{Ne}}{\partial y} x & -\frac{\partial \hat{V}_{Ne}}{\partial z} x \\ -\frac{\partial \hat{V}_{Ne}}{\partial x} y & \frac{\partial \hat{V}_{Ne}}{\partial x} x + \frac{\partial \hat{V}_{Ne}}{\partial z} z & -\frac{\partial \hat{V}_{Ne}}{\partial z} y \\ -\frac{\partial \hat{V}_{Ne}}{\partial x} z & -\frac{\partial \hat{V}_{Ne}}{\partial y} z & \frac{\partial \hat{V}_{Ne}}{\partial x} x + \frac{\partial \hat{V}_{Ne}}{\partial y} y \end{pmatrix}$$

The tensor components of the orbital operators contained in (7) are

$$\begin{aligned} l_{E,x} &= l_y, \quad l_{E,y} = -l_x, \quad l_{A_2} = l_z \\ G_{1,A_1} &= \frac{\partial \hat{V}_{Ne}}{\partial x} x + \frac{\partial \hat{V}_{Ne}}{\partial y} y, \quad G_{2,A_1} = \frac{\partial \hat{V}_{Ne}}{\partial z} z, \\ G_{1,E,x} &= \frac{\partial \hat{V}_{Ne}}{\partial x} x - \frac{\partial \hat{V}_{Ne}}{\partial y} y, \quad G_{2,E,x} = \frac{\partial \hat{V}_{Ne}}{\partial z} x, \\ G_{3,E,x} &= \frac{\partial \hat{V}_{Ne}}{\partial x} z, \quad G_{1,E,y} = -\frac{\partial \hat{V}_{Ne}}{\partial x} y - \frac{\partial \hat{V}_{Ne}}{\partial y} x, \\ G_{2,E,y} &= \frac{\partial \hat{V}_{Ne}}{\partial z} y, \quad G_{3,E,y} = \frac{\partial \hat{V}_{Ne}}{\partial y} z \end{aligned} \quad (9)$$

Hence, using the general matrix representations of table II, the matrix representation of the magnetic interaction (7) with the ground triplet can be obtained correct to first-order in the spin coupling coefficients

$$V_{\text{mag}} = \mu_B \begin{pmatrix} 0 & ig_{\perp} B_y & -ig_{\perp} B_x \\ -ig_{\perp} B_y & 0 & -ig_{\parallel} B_z \\ ig_{\perp} B_x & ig_{\parallel} B_z & 0 \end{pmatrix} \quad (10)$$

where

$$\begin{aligned} g_{\perp} &= g_e + (s_{2,6} - \frac{s_{1,8}}{\sqrt{2}}) l_{a,E} + \frac{1}{2} g_{1,A_1} + g_{2,A_1}, \\ g_{\parallel} &= g_e + g_{1,A_1} \end{aligned} \quad (11)$$

and $l_{a,E} = -i \langle a_1 | l_E | e \rangle / \sqrt{2} \hbar$, $g_{1,A_1} = \langle e | G_{1,A_1} | e \rangle / 2m_e c^2$ and $g_{2,A_1} = \langle e | G_{2,A_1} | e \rangle / 2m_e c^2$. Given that the relativistic term (8) is much smaller than the non-relativistic term, only contributions of the relativistic term that are zero-order in the spin coupling coefficients have been included.

Comparing (10) with the matrix representations of the total spin operators in table II, it can be seen that the magnetic interaction can be written in the spin-Hamiltonian form $\hat{V}_{\text{mag}} = \frac{\mu_B}{\hbar} \vec{S} \cdot \vec{g} \cdot \vec{B}$, where the effective g-factor tensor \vec{g} is defined as

$$\vec{g} = \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix} \quad (12)$$

The parameters g_{\perp} and g_{\parallel} may then be identified as the non-axial and axial effective g-factor components respectively. The g-factor components have been measured by several ESR studies^{33,43,44} and the observed values are contained in table III. The measurements conclusively show that both g_{\parallel} and g_{\perp} are shifted by $+6 \pm 1 \times 10^{-4}$ from the free electron g-factor $g_e = 2.0023$ and one

TABLE II: Matrix representations of the components of the total spin operator $\vec{S} = \sum_i \vec{s}_i$ and the orbital tensor operators $\hat{O}_{p,q} = \sum_i \hat{O}_{p,q}(\vec{r}_i)$ of different symmetry (p, q) correct to first-order in the spin coupling coefficients in the basis of the corrected spin-orbit states $\{\Phi_{1,A_1}^{so'}, \Phi_{2,E,x}^{so'}, \Phi_{2,E,y}^{so'}\}$ of the ground triplet. The orbital parameters in terms of reduced matrix elements of the center's molecular orbitals are $o_{a,A_1} = 2(\langle a_1 | \hat{O}_{A_1} | a_1 \rangle + \langle e | \hat{O}_{A_1} | e \rangle)$ and $o_{a,E} = \langle a_1 | \hat{O}_{A_1} | e \rangle$.

$$\begin{aligned}
 S_x &= \begin{pmatrix} 0 & 0 & -i\hbar \\ 0 & 0 & 0 \\ i\hbar & 0 & 0 \end{pmatrix} \quad S_y = \begin{pmatrix} 0 & i\hbar & 0 \\ -i\hbar & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad S_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i\hbar \\ 0 & i\hbar & 0 \end{pmatrix} \\
 \hat{O}_{A_1} &= \begin{pmatrix} o_{a,A_1} & 0 & 0 \\ 0 & o_{a,A_1} & 0 \\ 0 & 0 & o_{a,A_1} \end{pmatrix} \quad \hat{O}_{A_2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 \hat{O}_{E,x} &= \begin{pmatrix} 0 & s_{2,6}o_{a,E} + \frac{s_{1,8}}{\sqrt{2}}o_{a,E}^* & 0 \\ s_{2,6}o_{a,E}^* + \frac{s_{1,8}}{\sqrt{2}}o_{a,E} & -\frac{1}{\sqrt{2}}s_{2,5}(o_{a,E} + o_{a,E}^*) & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}}s_{2,5}(o_{a,E} + o_{a,E}^*) \end{pmatrix} \\
 \hat{O}_{E,y} &= \begin{pmatrix} 0 & 0 & s_{2,6}o_{a,E} + \frac{s_{1,8}}{\sqrt{2}}o_{a,E}^* \\ 0 & 0 & \frac{1}{\sqrt{2}}s_{2,5}(o_{a,E} + o_{a,E}^*) \\ s_{2,6}o_{a,E}^* + \frac{s_{1,8}}{\sqrt{2}}o_{a,E} & \frac{1}{\sqrt{2}}s_{2,5}(o_{a,E} + o_{a,E}^*) & 0 \end{pmatrix}
 \end{aligned}$$

study⁴⁴ observed a small anisotropy of $g_{\perp} - g_{\parallel} = 2 \times 10^{-4}$. From (11) it is clear that there is no orbital magnetic moment contribution to g_{\parallel} at first-order in the spin coupling coefficients and due to the expected orders of magnitudes of the coefficients, any second-order contribution would be much smaller than the observed shifts of g_{\parallel} and g_{\perp} . Thus, only the relativistic term (8) which shifts g_{\parallel} from g_e by the addition of g_{1,A_1} and also shifts g_{\perp} by the addition of $\frac{1}{2}g_{1,A_1} + g_{2,A_1}$, can explain the observed shifts. The different contributions of the relativistic term to g_{\perp} and g_{\parallel} can also explain the small anisotropy, however if the orbital magnetic moment contribution to g_{\perp} is large enough, it may also contribute at the same order as the relativistic term. The leading order term of the orbital magnetic moment contribution to g_{\perp} is

$$(s_{2,6} - \frac{s_{1,8}}{\sqrt{2}})l_{a,E} \approx 2 \frac{\lambda_{\perp}}{E_{E;1}} l_{a,E} \quad (13)$$

due to the expectation that $\lambda_{\perp} \gg \eta D_{1,E,2}$. Through the observation of the magnetic circular dichroism (MCD) of the optical ZPL,²³ the orbital magnetic moment parameter will be of the order $l_{a,E} \sim 10^{-1}$. Consequently, the orbital magnetic moment will only contribute significantly to the g-factor anisotropy if $2 \frac{\lambda_{\perp}}{E_{E;1}} \sim 10^{-3}$, which given $E_{E;1} \approx 2.180$ eV,²² implies that λ_{\perp} would have to be of the order of 1 meV ~ 1 THz, a dramatic difference from the axial spin-orbit parameter $\lambda_{\parallel} = 5.3$ GHz. Such a dramatic difference is improbable given the NV⁻ center's small departure from the higher T_d symmetry, in which the axial and non-axial spin-orbit parameters are equal. Therefore, it appears unlikely that the orbital magnetic moment contributes significantly to \bar{g} .

B. Interactions with electric fields

Defining \vec{E} to be the applied electric field that is assumed to be approximately constant over the dimensions

of the NV⁻ center, the interaction of the center's electrons with the electric field is described by the potential⁵²

$$\hat{V}_{el} = \sum_i \vec{d}_i \cdot \vec{E} \quad (14)$$

where $\vec{d} = e\vec{r}$ is the electron electric dipole moment. The tensor components of \vec{d} are simply $\vec{d} = d_{E,x}\vec{x} + d_{E,y}\vec{y} + d_{A_1}\vec{z}$ and the ground triplet matrix representation of \hat{V}_{el} correct to first-order in the spin coupling coefficients is

$$V_{el} = \begin{pmatrix} d_{a,A_1}E_z & d'_{\perp}E_x & d'_{\perp}E_y \\ d'_{\perp}E_x & d_{a,A_1}E_z + d_{\perp}E_x & -d_{\perp}E_y \\ d'_{\perp}E_y & -d_{\perp}E_y & d_{a,A_1}E_z - d_{\perp}E_x \end{pmatrix} \quad (15)$$

where $d_{a,A_1} = 2(\langle a_1 | d_{A_1} | a_1 \rangle + \langle e | d_{A_1} | e \rangle)$, $d_{\perp} = -2s_{2,5}d_{a,E}$, $d'_{\perp} = (s_{2,6} + \frac{s_{1,8}}{\sqrt{2}})d_{a,E}$ and $d_{a,E} = \frac{1}{\sqrt{2}}\langle a_1 | d_E | e \rangle$.

The leading order terms of the two non-axial dipole parameters are

$$d_{\perp} \approx 2 \frac{\eta \lambda_{\perp}}{E_{E;1}} d_{a,E}, \quad d'_{\perp} \approx -2 \frac{D_{1,E,2}}{E_{E;1}} d_{a,E} \quad (16)$$

which due to the potentially similar orders of magnitude of the numerators in each, suggests that the parameters are potentially of the same magnitude. However, since d'_{\perp} couples electronic states separated in energy by D_{gs} , it can be ignored for static electric fields that satisfy $d'_{\perp}E_{\perp} \ll D_{gs}$, where $E_{\perp} = \sqrt{E_x^2 + E_y^2}$ is the non-axial electric field strength. This conclusion is in agreement with observation,^{9,30} where small linear Stark splittings of the $m_s = \pm 1$ fine structure levels have been shown to agree with $d'_{\perp} \approx 0$ and $d_{\perp}/h = 17 \pm 3$ Hz cm/V.³⁰

Since correct to first-order in the spin coupling coefficients, the term $d_{a,A_1}E_z$ is common to each of the diagonal matrix elements, it appears that an axial electric

TABLE III: Experimental measurements and *ab initio* calculations of the effective g-factor and hyperfine parameters of the NV⁻ center tabulated by reference.

| Ref. | g_{\perp} | g_{\parallel} | A_{\perp}/h (MHz) | A_{\parallel}/h (MHz) | P/h (MHz) |
|---|-------------|-----------------|---------------------|--------------------------|---------------------|
| Loubser ⁴³ (Exp) | 2.0028(3) | 2.0028(3) | - | (\pm)2.32 \pm 0.01 | - |
| He ³³ (Exp) | 2.0028(3) | 2.0028(3) | (+)2.10 \pm 0.10 | (+)2.30 \pm 0.02 | (-)5.04 \pm 0.05 |
| Felton ⁴⁴ (Exp) | 2.0031(2) | 2.0029(2) | (-)2.70(7) | (-)2.14(7) | (-)5.01(6) |
| Steiner ⁴⁵ (Exp) | - | - | - | -2.166 \pm 0.01 | -4.945 \pm 0.01 |
| Smeltzer ⁴⁶ (Exp) | - | - | - | -2.162(2) | -4.945(5) |
| Gali ⁴² (<i>Ab initio</i>) | - | - | (-)1.7 | (-)1.7 | - |

field does not induce a relative shift of the fine structure levels of the ground triplet. However, this conclusion is in conflict with observation,³⁰ where a very small linear shift of the zero-field splitting between the $m_s = 0$ and $m_s = \pm 1$ fine structure levels was observed and could be described only by a difference of $d_{\parallel}/h = 0.35 \pm 0.02$ Hz cm/V in the axial dipole parameters of the $m_s = 0$ and $m_s = \pm 1$ spin-orbit states. Such a difference occurs at second-order in the spin coupling coefficients, where the matrix representation of the interaction of the ground triplet with an axial electric field becomes

$$d_{A_1} E_z = \begin{pmatrix} d_{a,A_1} E_z & 0 & 0 \\ 0 & (d_{a,A_1} + d_{\parallel}) E_z & 0 \\ 0 & 0 & (d_{a,A_1} + d_{\parallel}) E_z \end{pmatrix} \quad (17)$$

where $d_{\parallel} = (s_{2,5}^2 + s_{2,6}^2 + s_{2,9}^2) d_{b,A_1}$ and $d_{b,A_1} = \langle e || d_{A_1} || e \rangle - \langle a_1 || d_{A_1} || a_1 \rangle$. Therefore, the effective matrix representation of the interaction of the ground triplet with a static electric field satisfying $d'_{\perp} E_{\perp} \ll D_{gs}$ is

$$V_{el} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & d_{\parallel} E_z + d_{\perp} E_x & -d_{\perp} E_y \\ 0 & -d_{\perp} E_y & d_{\parallel} E_z - d_{\perp} E_x \end{pmatrix} \quad (18)$$

This effective representation can be expressed in the spin-Hamiltonian form $\hat{V}_{el} = \frac{1}{\hbar^2} d_{\parallel} E_z S_z^2 - \frac{1}{\hbar^2} d_{\perp} E_x (S_x^2 - S_y^2) + \frac{1}{\hbar^2} d_{\perp} E_y (S_x S_y + S_y S_x)$ used to describe the linear Stark effect present in C_{3v} symmetric systems in ESR.⁵³

The dipole reduced matrix element $d_{a,E}$ contained in d_{\perp} is also responsible for the center's optical transition²² and an estimate of its magnitude can be obtained from the center's observed radiative lifetime $T_R \approx 13$ ns⁵⁴ using⁵⁵

$$d_{a,E}/h = \left(\frac{6\pi\epsilon_0 \hbar^4 c^3}{\langle E_O^3 \rangle n_D T_R} \right)^{\frac{1}{2}} / h \quad (19)$$

where $\langle E_O^3 \rangle = \int_0^{\infty} F(E_O) E_O^3 dE_O$ is the expectation value of the cube of the optical emission energy given the normalized vibrational sideband distribution $F(E_O)$,⁵⁶ and $n_D = 2.418$ is the refractive index of diamond. As the vibrational sideband of the center's optical emission extends from approximately 1.4 eV to the ZPL at 1.945 eV, the estimate of the dipole reduced matrix element is

bounded by $3.65 \leq d_{a,E}/h \leq 5.98$ MHz cm/V (compare with, for example, the 5.41 MHz cm/V dipole moment of the $5s(^2S_{1/2}) \longleftrightarrow 5p(^2P_{3/2})$ transition of ⁸⁷Rb).⁵⁷

The observed value of $d_{\perp}/h = 17 \pm 3$ Hz cm/V,³⁰ the estimated range of $d_{a,E}$, the approximate expression for $d_{\perp} \approx 2 \frac{\eta \lambda_{\perp}}{E_{E;1}} d_{a,E}$, and $\eta = 0.053$,²² imply that $\frac{\lambda_{\perp}}{E_{E;1}} \sim 10^{-4}$ as expected, thereby supporting the assertion made in the previous subsection that the orbital magnetic moment does not contribute significantly to \bar{g} . The dipole reduced matrix element d_{b,A_1} contained in d_{\parallel} also contributes to the shift of the center's optical ZPL in the presence of an axial electric field.²² However, since the optical transition involves a change in MO configuration and, thus a change in the nuclear equilibrium coordinates,²² both the axial electric and nuclear dipole moments contribute to the shift of the center's optical ZPL. Consequently, without knowledge of the nuclear dipole moment, it is not possible to estimate d_{b,A_1} given just measurements of the shift.

C. Interactions with strain fields

The interaction of the center's electrons with a crystal strain field can be approximately described by performing a Taylor series expansion of the electronic Hamiltonian \hat{H}_e in terms of the displacements of the nuclear coordinates \vec{R} from their ground state equilibrium coordinates \vec{R}_0 induced by the strain field and retaining only the linear terms of the expansion. Defining $Q_{u,p,q}$ to be the u^{th} normal nuclear displacement coordinate of the crystal that transforms as the row q of the irreducible representation p of the C_{3v} group, the strain potential is⁵⁵

$$\hat{V}_{str} = \sum_i \sum_{u,p,q} \frac{\partial \hat{V}_{Ne}(\vec{r}_i, \vec{R})}{\partial Q_{u,p,q}} \bigg|_{\vec{R}_0} \xi_{u,p,q} \quad (20)$$

where $\xi_{u,p,q}$ is the crystal strain along the displacement coordinate $Q_{u,p,q}$. Given that by definition $\partial \hat{V}_{Ne}(\vec{r}_i, \vec{R}) / \partial Q_{u,p,q} |_{\vec{R}_0}$ is an orbital tensor operator of symmetry (p, q) , the ground triplet matrix representation of \hat{V}_{str} is analogous to that of \hat{V}_{el} . Treating the non-axial terms correct to first-order and the axial terms correct to second-order in the spin coupling coefficients,

the matrix representation of \hat{V}_{str} is

$$V_{str} = \begin{pmatrix} \zeta'_z & \zeta'_x & \zeta'_y \\ \zeta'_x & \zeta'_z + \zeta_x & -\zeta_y \\ \zeta'_y & -\zeta_y & \zeta'_z + \zeta_z - \zeta_x \end{pmatrix} \quad (21)$$

where

$$\begin{aligned} \zeta'_z &= \sum_u \zeta_{u,a,A1} \xi_{u,A1} \\ \zeta_z &= (s_{2,5}^2 + s_{2,6}^2 + s_{2,9}^2) \sum_u \zeta_{u,b,A1} \xi_{u,A1} \\ \zeta'_k &= (s_{2,6} + \frac{s_{1,8}}{\sqrt{2}}) \sum_u \zeta_{u,a,E} \xi_{u,E,k} \\ \zeta_k &= -2s_{2,5} \sum_u \zeta_{u,a,E} \xi_{u,E,k} \\ \zeta_{u,a,A1} &= 2\langle a_1 | \left| \frac{\partial \hat{V}_{Ne}}{\partial Q_{u,A1}} \right|_{\vec{R}_0} | a_1 \rangle + 2\langle e | \left| \frac{\partial \hat{V}_{Ne}}{\partial Q_{u,A1}} \right|_{\vec{R}_0} | e \rangle \\ \zeta_{u,b,A1} &= \langle e | \left| \frac{\partial \hat{V}_{Ne}}{\partial Q_{u,A1}} \right|_{\vec{R}_0} | e \rangle - \langle a_1 | \left| \frac{\partial \hat{V}_{Ne}}{\partial Q_{u,A1}} \right|_{\vec{R}_0} | a_1 \rangle \\ \zeta_{u,a,E} &= \frac{1}{\sqrt{2}} \langle a_1 | \left| \frac{\partial \hat{V}_{Ne}}{\partial Q_{u,E}} \right|_{\vec{R}_0} | e \rangle \end{aligned} \quad (22)$$

and $k = x, y$. Note that torsional strain components that have displacement coordinates that transform as A_2 have been ignored.

Similar to \hat{V}_{el} , the diagonal contributions ζ'_z do not shift the fine structure levels of the ground triplet with respect to each other and thus can be effectively ignored. Likewise, for non-axial strains that satisfy $\zeta'_\perp \ll D_{gs}$ (where $\zeta'_\perp = \sqrt{\zeta'^2_x + \zeta'^2_y}$), ζ'_x and ζ'_y will have negligible effect on the fine structure levels and state coupling and thus can also be ignored. Defining the effective strain field $\vec{\sigma} = \sigma_x \vec{x} + \sigma_y \vec{y} + \sigma_z \vec{z} = \zeta_x/d_\perp \vec{x} + \zeta_y/d_\perp \vec{y} + \zeta_z/d_\parallel \vec{z}$, the effective matrix representation of \hat{V}_{str} becomes

$$V_{str} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & d_\parallel \sigma_z + d_\perp \sigma_x & -d_\perp \sigma_y \\ 0 & -d_\perp \sigma_y & d_\parallel \sigma_z - d_\perp \sigma_x \end{pmatrix} \quad (23)$$

and it is clear that the strain field can be treated as an additional effective local electric field $\vec{\sigma}$ at the center. Hence, by defining the total effective electric field $\vec{\Pi} = \vec{E} + \vec{\sigma}$, the interaction of the center with both strain and electric fields can be expressed in the spin-Hamiltonian form $\hat{V}_{el} + \hat{V}_{str} = \frac{1}{\hbar^2} d_\parallel \Pi_z S_z^2 - \frac{1}{\hbar^2} d_\perp \Pi_x (S_x^2 - S_y^2) + \frac{1}{\hbar^2} d_\perp \Pi_y (S_x S_y + S_y S_x)$.

D. The complete spin-Hamiltonian

Including the descriptions of the spin-spin zero-field splitting and interactions with magnetic, electric and strain fields obtained in the previous subsections, the

complete electronic spin-Hamiltonian of the ground state spin becomes

$$\begin{aligned} \hat{H}_{gs} &= \frac{1}{\hbar^2} (D_{gs} + d_\parallel \Pi_z) S_z^2 + \frac{\mu_B}{\hbar} \vec{S} \cdot \vec{g} \cdot \vec{B} \\ &\quad - \frac{1}{\hbar^2} d_\perp \Pi_x (S_x^2 - S_y^2) + \frac{1}{\hbar^2} d_\perp \Pi_y (S_x S_y + S_y S_x) \end{aligned} \quad (24)$$

which in the spin basis $\{S_{A_2}, -S_{E,y}, S_{E,x}\}$ associated with the ground triplet spin-orbit states, has the matrix representation

$$\hat{H}_{gs} = \begin{pmatrix} 0 & i\mathcal{B}_y & -i\mathcal{B}_x \\ -i\mathcal{B}_y & \mathcal{D} + \mathcal{E}_x & -i\mathcal{B}_z - \mathcal{E}_y \\ i\mathcal{B}_x & i\mathcal{B}_z - \mathcal{E}_y & \mathcal{D} - \mathcal{E}_x \end{pmatrix} \quad (25)$$

where $\mathcal{D} = D_{gs} + d_\parallel \Pi_z$, $\mathcal{B}_z = \mu_B g_\parallel B_z$, $\mathcal{E}_k = d_\perp \Pi_k$, $\mathcal{B}_k = \mu_B g_\perp B_k$, and $k=x,y$. This final matrix representation provides the simplest description of the dependence of the ground state spin on the six independent electric-magnetic-strain field parameters $(\mathcal{D}, \mathcal{E}_x, \mathcal{E}_y, \vec{\mathcal{B}})$ and will be used to obtain the spin solution in part II of this paper series.⁵⁹

III. NUCLEAR HYPERFINE STRUCTURE

The nuclear hyperfine interaction $\hat{V}_{hf} = \hat{V}_{mhf} + \hat{V}_{ehf}$ between the center's electrons and the nuclei of the crystal lattice has magnetic \hat{V}_{mhf} and electric \hat{V}_{ehf} components. The magnetic hyperfine component accounts for the interactions of the electronic spin and orbital magnetic moment with the nuclear spins of the lattice. Since it was found in the previous section that the ground triplet has no orbital magnetic moment at zero-order in the spin coupling coefficients, the interaction between the orbital magnetic moment and the nuclear spins maybe ignored. The electric hyperfine component approximately accounts for the finite size of the nuclei through the interaction of the center's electrons with the electric quadrupole moments of the finite charge distributions of the nuclei. In an isotopically pure ^{12}C crystal, only the ^{14}N nucleus of the center will have a non-zero nuclear spin ($I = 1$) and a non-zero electric quadrupole moment.⁵⁵ Consequently, in an isotopically pure crystal the magnetic and electric hyperfine interactions of the NV^- center are described by the potentials⁵⁵

$$\begin{aligned} \hat{V}_{mhf} &= C_{mhf} \sum_i \left(4\pi \delta(\vec{r}_{iN}) - \frac{1}{|\vec{r}_{iN}|^3} \right) \vec{s}_i \cdot \vec{I} \\ &\quad + \frac{3(\vec{s}_i \cdot \vec{r}_{iN})(\vec{r}_{iN} \cdot \vec{I})}{|\vec{r}_{iN}|^5} \\ \hat{V}_{ehf} &= \frac{1}{2Z_N} \sum_{\alpha,a,b} \left(\sum_i \frac{\partial^2 \hat{V}_e(\vec{r}_i)}{\partial R_{N,a} \partial R_{N,b}} \right)_{\vec{R}_0} \\ &\quad + \frac{\partial^2 V_l}{\partial R_{N,a} \partial R_{N,b}} \Big|_{\vec{R}_0} u_{\alpha,a} u_{\alpha,b} \end{aligned} \quad (26)$$

where $C_{mhf} = \mu_B \mu_N g_N \frac{\mu_0}{4\pi\hbar^2}$, μ_N is the nuclear magneton, $g_N = 0.40356$ is the ^{14}N nuclear g-factor,⁵² \vec{I} is the spin operator of the ^{14}N nucleus, $\vec{r}_{iN} = \vec{R}_N - \vec{r}_i = x_{iN}\vec{x} + y_{iN}\vec{y} + z_{iN}\vec{z}$, $\vec{R}_N = R_{N,x}\vec{x} + R_{N,y}\vec{y} + R_{N,z}\vec{z}$ is the position of the ^{14}N nucleus, \hat{V}_e is the Coulomb interaction potential of the center's electrons with the ^{14}N nucleus, V_l is the Coulomb interaction potential of the lattice electrons and ^{12}C nuclei with the ^{14}N nucleus, $Z_N = 7$ is the relative charge of the ^{14}N nucleus, and $u_{\alpha,a}$ and $u_{\alpha,b}$ are the components of the displacement of the α^{th} ^{14}N proton from \vec{R}_N in the $a, b = x, y, z$ directions.

The magnetic hyperfine interaction can be written as a sum of terms containing rank two orbital tensor operators $\hat{V}_{mhf} = \sum_i \vec{s}_i \cdot [\vec{A}_{A_1}(r_{iN}) + \vec{A}_{E,x}(r_{iN}) + \vec{A}_{E,y}(r_{iN})] \cdot \vec{I}$. By applying the matrix representations of table II, it is clear that only the term containing $\vec{A}_{A_1}(r_{iN})$ contributes at zero-order in the spin coupling coefficients. Given this result, \hat{V}_{mhf} can be written in the spin-Hamiltonian form $\hat{V}_{mhf} = \vec{S} \cdot \vec{A} \cdot \vec{I}$, where

$$\vec{A} = \begin{pmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{pmatrix},$$

$A_{\parallel} = f_{A_1} + 2a_{A_1}$ is the axial magnetic hyperfine parameter, $A_{\perp} = f_{A_1} - a_{A_1}$ is the non-axial magnetic hyperfine parameter, $f_{A_1} = C_{mhf}4\pi\langle e||\delta(\vec{r}_{iN})||e\rangle$ is the Fermi contact contribution, and $a_{A_1} = \frac{1}{2}C_{mhf}\langle e||\frac{1}{|\vec{r}_{iN}|^3}\left(\frac{3z_{iN}^2}{|\vec{r}_{iN}|^2} - 1\right)||e\rangle$ is the dipolar contribution. Measured values of the magnetic hyperfine parameters are contained in table III and, although they differ in sign and magnitude, conclusively show that both the Fermi contact and dipolar contributions must be non-zero. For example, using the values obtained in Ref. 44, $f_{A_1}/h = -2.51$ MHz and $a_{A_1}/h = 187$ kHz.

The expression for the Fermi contact contribution can be simplified further to $f_{A_1} = C_{mhf}4\pi|e_x(\vec{R}_N)|^2 = C_{mhf}4\pi|e_y(\vec{R}_N)|^2$. As the e MOs transform as the E irreducible representation of the C_{3v} group, they are by definition zero at any point along the axial symmetry axis of the center, and since the equilibrium position of the ^{14}N nucleus is on the axial symmetry axis, the Fermi contact contribution vanishes if the ^{14}N is fixed at its equilibrium position. To account for the non-zero Fermi contact contribution in the molecular model, the vibrational wavefunction $\chi_N(\vec{R}_N)$ of the ^{14}N must be considered, in which case the expression for the Fermi contact contribution becomes

$$f_{\text{vib}} = C_{mhf}4\pi \int |e_x(\vec{R}_N)|^2 |\chi_N(\vec{R}_N)|^2 d^3R_N \quad (27)$$

A similar vibrationally corrected expression for the dipolar contribution can also be defined.

The magnetic polarization of the ^{14}N core electrons associated with the $m_s = \pm 1$ states of the center will provide a negative Fermi contact contribution f_{core} ^{42,44}

in addition to the positive contribution arising from the vibrational motion of the nucleus. However, the description of f_{core} is beyond the molecular model in its current formulation, as only the interactions of the bound valence electrons are considered in the model. An *ab initio* study⁴² has yielded $f_{\text{core}} \approx -1.7$ MHz, but no *ab initio* calculation of the vibrationally corrected f_{vib} has been conducted to date. Although f_{vib} is likely to be much smaller than f_{core} , the calculation of f_{vib} will provide a more complete *ab initio* model of the magnetic hyperfine parameters. Likewise, an extension of the molecular model to describe f_{core} will also provide further insight into the interactions between the nucleus and the bound electrons.

The electronic component of the electric hyperfine interaction \hat{V}_{ehf} can be written as a sum of products of orbital electronic and nuclear tensor operators. Analogous to the interaction of the ground state spin with electric and strain fields, at zero-order in the spin coupling coefficients only the terms of \hat{V}_{ehf} that contain A_1 orbital electronic tensor operators will have non-zero matrix elements, and these matrix elements will be diagonal and identical for each spin state. The symmetry of the lattice ensures that only similar terms from the lattice electron and internuclear contribution are also non-zero. Consequently, the electric hyperfine interaction within the ground state spin reduces to

$$\hat{V}_{ehf} = \frac{q_z}{4Z_N} \sum_{\alpha} 3u_{\alpha,z}^2 - |\vec{u}_{\alpha}|^2 \quad (28)$$

where $q_z = 2\langle e||\partial^2\hat{V}_e/\partial R_{N,z}^2|\vec{R}_0||e\rangle + 2\langle a_1||\partial^2\hat{V}_e/\partial R_{N,z}^2|\vec{R}_0||a_1\rangle + \partial^2V_l/\partial R_{N,z}^2|\vec{R}_0|$ is proportional to the axial gradient of the net axial electric field at the ^{14}N nucleus generated by all of the electrons and other nuclei.

As per standard practice, the nuclear quadrupole operator $\sum_{\alpha} 3u_{\alpha,z}^2 - |\vec{u}_{\alpha}|^2$ can be replaced by a nuclear spin operator $Q_z I_z^2/\hbar^2$ of the same symmetry through the definition of the proportionality constant $Q_z = \langle 1, 1|\sum_{\alpha} 3u_{\alpha,z}^2 - |\vec{u}_{\alpha}|^2|1, 1\rangle$ using the I_z eigenstate $|I = 1, m_I = 1\rangle$.⁵⁸ Q_z therefore quantifies the difference in the axial anisotropy of the nuclear quadrupole moment between the $m_I = \pm 1$ and $m_I = 0$ states. The final form of the effective electric hyperfine interaction is then $\hat{V}_{ehf} = P I_z^2/\hbar^2$, where $P = q_z Q_z/4Z_N$ is the nuclear quadrupole parameter contained in table III.

Combining the expressions obtained for the magnetic and electric hyperfine interactions, the zero-field spin-Hamiltonian of the ground state spin including nuclear hyperfine interaction is

$$\hat{H}_{hf} = \frac{1}{\hbar^2} [D_{gs} S_z^2 + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) + P I_z^2] \quad (29)$$

The approximate solutions of \hat{H}_{hf} can be obtained by constructing the hyperfine states of the ground triplet

in a similar manner to the earlier construction of the electronic spin-orbit states by defining linear combinations of products of electronic spin-orbit and nuclear spin states that have definite C_{3v} symmetry. Given that the symmetrised nuclear spin states of the ^{14}N nucleus in terms of the I_z eigenstates $\{|I, m_I\rangle\}$ are $I_{A_2} = |1, 0\rangle$, $I_{E,x} = \frac{-i}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle)$ and $I_{E,y} = \frac{-1}{\sqrt{2}}(|1, 1\rangle - |1, -1\rangle)$, the symmetrised hyperfine states $\Psi_{n,j,k}$ are

$$\begin{aligned}\Psi_{1,E,x} &= \Phi_{1,A_1}^{so} I_{E,x}, \quad \Psi_{1,E,y} = \Phi_{1,A_1}^{so} I_{E,y} \\ \Psi_{2,A_2} &= \Phi_{2,A_1}^{so} I_{A_2} \\ \Psi_{3,E,x} &= \frac{1}{\sqrt{2}}(\Phi_{2,E,x}^{so} I_{E,x} - \Phi_{2,E,y}^{so} I_{E,y})\end{aligned}$$

$$\begin{aligned}\Psi_{3,E,y} &= \frac{-1}{\sqrt{2}}(\Phi_{2,E,x}^{so} I_{E,y} - \Phi_{2,E,y}^{so} I_{E,x}) \\ \Psi_{4,A_1} &= \frac{1}{\sqrt{2}}(\Phi_{2,E,x}^{so} I_{E,x} + \Phi_{2,E,y}^{so} I_{E,y}) \\ \Psi_{5,A_2} &= \frac{1}{\sqrt{2}}(\Phi_{2,E,x}^{so} I_{E,y} - \Phi_{2,E,y}^{so} I_{E,x}) \\ \Psi_{6,E,x} &= -\Phi_{2,E,y}^{so} I_{A_2}, \quad \Psi_{6,E,y} = \Phi_{2,E,x}^{so} I_{A_2}\end{aligned}\quad (30)$$

The matrix representation of the zero-field Hamiltonian in the basis of hyperfine states $\{\Psi_{2,A_2}, \Psi_{6,E,x}, \Psi_{6,E,y}, \Psi_{1,E,x}, \Psi_{1,E,y}, \Psi_{3,E,x}, \Psi_{3,E,y}, \Psi_{4,A_1}, \Psi_{5,A_2}\}$ is

$$H_{hf} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{2}A_{\perp} \\ 0 & D_{gs} & 0 & -A_{\perp} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{gs} & 0 & -A_{\perp} & 0 & 0 & 0 & 0 \\ 0 & -A_{\perp} & 0 & P & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -A_{\perp} & 0 & P & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & D_{gs} + h_{+} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & D_{gs} + h_{+} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & D_{gs} + h_{-} & 0 \\ \sqrt{2}A_{\perp} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & D_{gs} + h_{-} \end{pmatrix}\quad (31)$$

where $h_{\pm} = P \pm A_{\parallel}$. Note that the above basis of hyperfine states has been grouped into states of the same nuclear spin projection. The energies E_n^{hf} correct to first-order in nuclear hyperfine interactions can be easily inferred: $E_1^{hf} = P$, $E_2^{hf} = 0$, $E_3^{hf} = D_{gs} + P + A_{\parallel}$, $E_4^{hf} = E_5^{hf} = D_{gs} + P - A_{\parallel}$, $E_6^{hf} = D_{gs}$; and the corresponding hyperfine structure is depicted in Fig. 3. Since A_{\perp} is observed to satisfy $A_{\perp} \ll D_{gs}$,^{33,44} the non-

axial magnetic hyperfine parameter that couples hyperfine states of different nuclear spin projection will have a negligible effect on the zero-field hyperfine structure and state couplings.

The matrix representation of the electronic interaction with electric, magnetic and strain fields in the hyperfine basis is

$$V_{\text{mag}} + V_{\text{el}} + V_{\text{str}} = \begin{pmatrix} 0 & i\mathcal{B}_x & i\mathcal{B}_y & 0 & 0 & 0 & 0 & 0 & 0 \\ -i\mathcal{B}_x & d_{\parallel}\Pi_z - \mathcal{E}_x & \mathcal{E}_y - i\mathcal{B}_z & 0 & 0 & 0 & 0 & 0 & 0 \\ -i\mathcal{B}_y & i\mathcal{B}_z + \mathcal{E}_y & d_{\parallel}\Pi_z + \mathcal{E}_x & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{i\mathcal{B}_y}{\sqrt{2}} & \frac{i\mathcal{B}_x}{\sqrt{2}} & \frac{i\mathcal{B}_y}{\sqrt{2}} & \frac{i\mathcal{B}_x}{\sqrt{2}} \\ 0 & 0 & 0 & 0 & 0 & \frac{i\mathcal{B}_x}{\sqrt{2}} & -\frac{i\mathcal{B}_y}{\sqrt{2}} & -\frac{i\mathcal{B}_x}{\sqrt{2}} & \frac{i\mathcal{B}_y}{\sqrt{2}} \\ 0 & 0 & 0 & -\frac{i\mathcal{B}_y}{\sqrt{2}} & -\frac{i\mathcal{B}_x}{\sqrt{2}} & d_{\parallel}\Pi_z & i\mathcal{B}_z & \mathcal{E}_x & \mathcal{E}_y \\ 0 & 0 & 0 & -\frac{i\mathcal{B}_x}{\sqrt{2}} & \frac{i\mathcal{B}_y}{\sqrt{2}} & -i\mathcal{B}_z & d_{\parallel}\Pi_z & \mathcal{E}_y & -\mathcal{E}_x \\ 0 & 0 & 0 & -\frac{i\mathcal{B}_y}{\sqrt{2}} & \frac{i\mathcal{B}_x}{\sqrt{2}} & \mathcal{E}_x & \mathcal{E}_y & d_{\parallel}\Pi_z & i\mathcal{B}_z \\ 0 & 0 & 0 & -\frac{i\mathcal{B}_x}{\sqrt{2}} & -\frac{i\mathcal{B}_y}{\sqrt{2}} & \mathcal{E}_y & -\mathcal{E}_x & -i\mathcal{B}_z & d_{\parallel}\Pi_z \end{pmatrix}\quad (32)$$

The matrix representation demonstrates that if the much

smaller interaction of the nuclear spin with the fields is

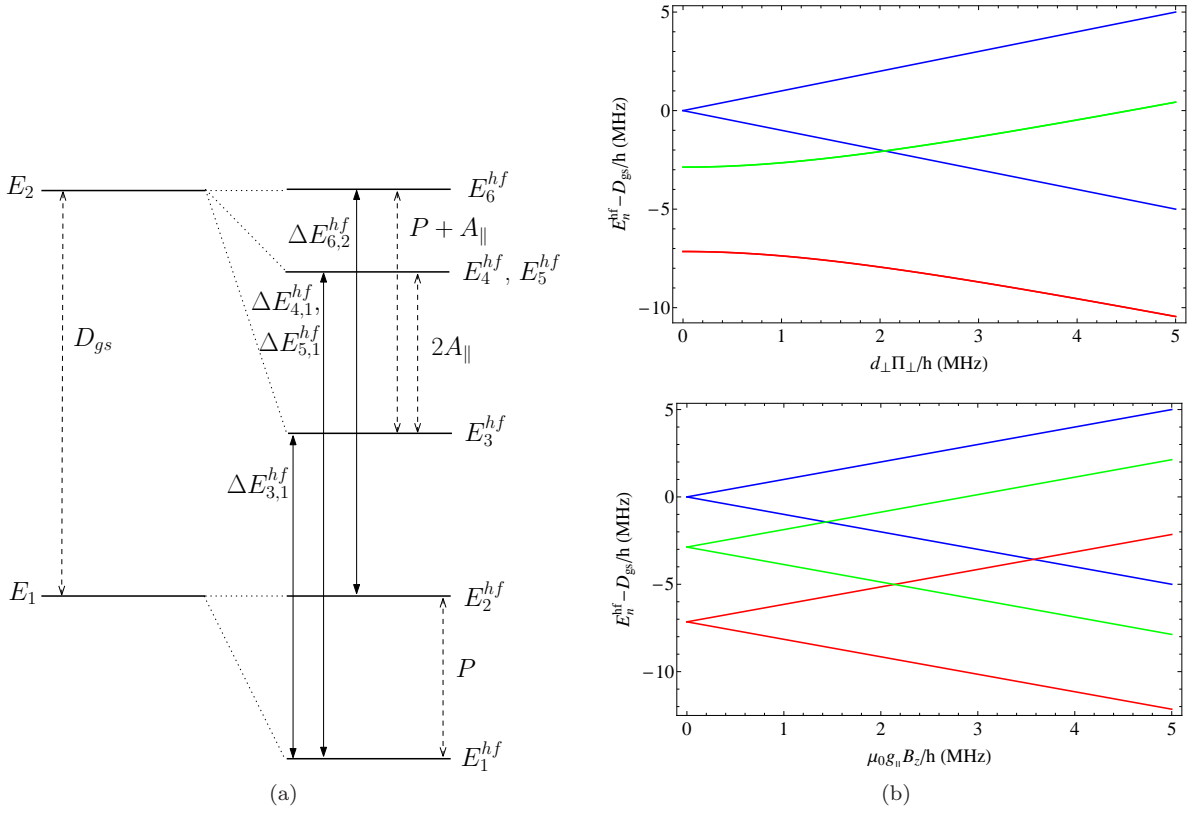


FIG. 3: (color online) (a) The hyperfine structure of the ground triplet. The level splittings are indicated by dashed arrows and the observed values for the hyperfine parameters A_{\parallel} and P are contained in table III. The ordering of the hyperfine levels is based upon the parameters measured in Ref. 44. The allowed magnetic transitions between levels of the same nuclear spin projection are indicated by solid arrows and labeled by their transition energy $\Delta E_{n,m}^{hf}$. (b) The splittings of the $m_s = \pm 1$ hyperfine levels in the presence of non-axial electric-strain fields of magnitude Π_{\perp} (upper) and axial magnetic fields B_z (lower). $m_I = 0$ hyperfine levels are colored blue and $m_I = \pm 1$ hyperfine levels are colored red and green. The hyperfine parameters of Ref. 44 have been used to calculate the splittings.

ignored, the fields do not couple states of different nuclear spin projection. Furthermore, by comparing the above matrix representation with that of \hat{H}_{gs} , the representation also demonstrates that the hyperfine states of nuclear spin projection $m_I = 0$ (upper 3×3 diagonal block) interact with the fields in a manner similar to the electronic spin-orbit states discussed in the previous section, whereas the $m_I = \pm 1$ hyperfine states (lower 6×6 diagonal block) interact differently in the weak field limit, where the fields induce shifts comparable to the hyperfine splittings. For example, as depicted in Fig. 3, the $(m_s = \pm 1, m_I = 0)$ states split linearly in the presence of a non-axial electric-strain field, whereas the non-degenerate $(m_s = \pm 1, m_I = \pm 1)$ states repel quadratically in the presence of non-axial electric-strain fields that satisfy $\mathcal{E}_{\perp} < 2A_{\parallel}$. Note that in the large field limit, where the fields induce shifts much larger than the hyperfine splittings, both sets of hyperfine states behave approximately analogous to the spin-orbit states.

The allowed magnetic transitions are depicted in Fig. 3 and indicate that in the absence of static fields, there

will exist three lines in the hyperfine spectra with energies $\Delta E_{3,1}^{hf} = D_{gs} + A_{\parallel}$, $\Delta E_{4,1}^{hf} = \Delta E_{5,1}^{hf} = D_{gs} - A_{\parallel}$ and $\Delta E_{6,2}^{hf} = D_{gs}$ in agreement with observation.⁴³ The central hyperfine line therefore corresponds to transitions between $m_I = 0$ states and the lower and higher energy lines correspond to transitions between $m_I = \pm 1$ states. Consequently, due to the different interactions of the $m_I = 0$ and $m_I = \pm 1$ states in the weak static field limit, the central hyperfine line will depend differently on the static fields compared to the lower and higher energy lines. These differences in the dependence of the hyperfine lines in the weak field limit was used in the recent electric field sensing demonstration,⁹ where the magnetic field was precisely aligned in the non-axial direction ($B_z = 0$) in the presence of a non-axial electric-strain field by observing the splitting of the $m_I = \pm 1$ hyperfine lines whilst the measurement of the electric field was conducted by observing the linear splitting of the central $m_I = 0$ hyperfine line. Hence, it is clear that the hyperfine structure of the ground state spin and its more complicated interactions with electric, magnetic and strain

fields, is an important consideration for applications of the spin that operate in the weak field limit.

IV. CONCLUSION

In this article, the theory of the ground state spin has for the first time been fully developed using the molecular model of the center in order to provide detailed explanations for the spin's fine and hyperfine structures and its interactions with electric, magnetic and strain fields. Given these explanations, an effective spin-Hamiltonian that describes the electronic states in the high field limit and the $m_I = 0$ subset of hyperfine states in the low field limit was derived. The explanations also allowed the correlation of the properties of the ground state spin with the other properties of the center and provided explicit expressions for the key parameters of spin in terms of

the center's MOs. Hence, this work has identified the critical parameters that need to be pursued by future experimental and *ab initio* studies. Furthermore, this work has also provided the essential theoretical understanding of this remarkable spin that can be used to model the spin in its ground-breaking quantum metrology and QIP applications.

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